



A Simple Fault-Finding Guide for Flame Atomic Absorption Spectrometry

Application Note

Atomic Absorption

Authors

Keith Brodie and Julie Rowland

Introduction

Atomic absorption spectrophotometers make it relatively easy to obtain analytical results which are consistently accurate and precise. Nonetheless, occasional operational problems can be encountered, and the causes may not be immediately obvious, especially to the less experienced operator. Most of these problems, however, can be solved by the operator or analyst without the need for a service call. This guide is designed to help in diagnosing such problems.



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Initial Set-Up

Your spectrophotometer cannot be expected to provide maximum analytical performance unless it is first set up correctly. Complete details of the setting up procedure are given in the instrument operation manual, but the following specific points are worth mentioning here:

- Ensure that the burner is completely clear of the optical path before attempting to align the hollow cathode lamp and adjust the monochromator.
- Ensure that the hollow cathode lamp is operating correctly at the recommended lamp current.
- Set the monochromator EXACTLY to the wavelength peak approaching from the low wavelength side. Note that some of the elements have complex spectra. Be particularly careful with the monochromator adjustment for these elements, otherwise the instrument will be set on the wrong wavelength.
- Select the recommended spectral band width.
- Align the hollow cathode lamp so that the maximum available light energy is directed along the optical path.

Before igniting the flame, move the burner close to the position required for the final AA measurement.

Use the following procedure:

1. Zero the instrument to read 0.000 Abs.
2. With the aid of a business card or paper, use the horizontal control to align the centre of the burner slot with respect to the light beam. Carefully move the burner vertically until it just commences to block the light beam. This position can be detected with the aid of the digital or peak meter readout. Again use the horizontal control, and ensure that the centre of the burner slot is aligned with the light beam. If this is not so, repeat the procedure.
3. The instrument should still read zero absorbance, for example the burner must not block the light path.

This position is the best burner location from which to commence an analytical measurement. Further “fine tuning” can only be carried out with the flame on and aspiration of a standard solution.

Optimization (Flame On)

Light the flame according to the operation manual, and aspirate a standard solution of the analyte element which will give an absorbance of between 0.1 and 0.8. Now carry out the following sequence:

1. Carefully adjust the burner position rotationally and horizontally (not vertically) to achieve the maximum absorbance.
2. Downward vertical movement of the burner may be necessary, especially with nitrous oxide acetylene elements. Do not raise the burner so that the light path is blocked.
3. Adjust the flame composition to give the desired absorbance.
4. Always adjust the position of the glass bead to give the maximum absorbance consistent with minimum noise. The optimum bead position can be readily established using a standard copper solution (5 mg/L), air-acetylene flame, wavelength 324.8 nm, 0.5 nm spectral bandwidth, lamp current 4 mA. It is recommended that the glass bead be positioned close to the nebulizer venturi before placing the whole assembly into the spray chamber. Then move the glass bead away from the venturi with the screwdriver adjustment (anticlockwise). This procedure eliminates the possibility of fouling the glass bead on the venturi and fracturing the glass.

This optimum position will be generally suitable for all elements and most applications. For a few analyses, however, the noise level may be unacceptably high and it will be necessary to readjust the glass bead for the specific application.

Fault Finding

Difficulties encountered in the operation of a flame AA can usually be categorized into four topics which are covered in this section.

Low Absorbance

Use the following sequence to check possible causes:

1. The nebulizer may be partially blocked and absorbance may therefore be lower than expected. Nebulizer blockage can occur if the solution being aspirated has a high dissolved solids content or if particulate matter is suspended

in solution. Seawater analysis and some clinical samples are good examples of these problems. You should not attempt to aspirate continuously, solutions which have a dissolved solid content of more than about 1—2% w/v. If the old style nebulizers are being used, clean the capillary with the cleaning wire provided. Aspirate distilled water through the nebulizer for approximately 15 minutes to ensure that the capillary and venturi are thoroughly cleaned. If the new (demountable) nebulizers are being used, the nebulizer can be disassembled and cleaned as described in the operation manual. To reduce risk of blocking, nebulize the sample alternately with the blank solution at intervals of approximately 15 seconds.

2. With the flame OFF, check that the nebulizer is fitted correctly by using a soap solution or a commercially available solution such as "Snoop" to check for gas leaks. Check around the nebulizer and bung for leaks. If leakages do exist, either tighten the appropriate clamps or remove the nebulizer from the bung and refit, following the installation instructions in the operation manual.
3. The plastic capillary tubing occasionally becomes blocked with dust or fluff from the surrounding atmosphere. Blockage will occur where the plastic capillary meets the nebulizer and the sample uptake rate will be severely reduced. Should this blockage occur, cut the end off the plastic capillary tube containing the dust particles and replace the tube on to the nebulizer.
4. The sample uptake rate can be measured by using a 10 mL calibrated cylinder, aspirating distilled water for 60 seconds and calculating the uptake rate. For a fixed nebulizer this should be between 4–6 mL per minute. When using an adjustable nebulizer the uptake control can vary the aspiration rate over the range of 0 to 10 mL per minute.

If the nebulizer does not meet these standards then parts may have worn out. With the new style nebulizers, disassemble and replace the worn parts as described in the operation manual. The old style nebulizers are not demountable and need to be replaced.

5. Careful adjustment of the glass bead is vital to ensure that the best absorbance is achievable. Once set, however, the same position will effectively apply to all elements.
6. Use the procedure outlined in Initial Set-Up and Optimization (Flame On) to achieve the burner position which will give the maximum absorbance. If the burner is too low or rotated about the optical path, low absorbance will result.

7. Check the flame stoichiometry. The chemical composition of a flame can have a marked effect on the decomposition process within the flame and can thus have a considerable effect on the characteristic concentration. It is therefore necessary to optimize the fuel-to-oxidant ratio for each element being analyzed. Elements such as barium, molybdenum and silicon require a reducing environment (a fuel-rich flame) to obtain maximum response. Other elements such as cadmium, copper and nickel require an oxidizing environment (that is, a fuel-lean flame). When adjusting flame conditions it is best to keep the oxidant flow constant and vary the fuel flow to obtain the maximum absorbance signal while aspirating the standard solution. If necessary, change the oxidant flow rate and again vary the fuel flow to obtain the desired absorbance.
8. Check the stability of solutions. When very dilute solutions of an element are being analyzed there is a high probability that the metal concentration of the solution will change over a short period of time. It is good practice to prepare fresh standards and solutions each day prior to each analysis. Standards should be prepared from stock solutions (typically 1000 mg/L) which contain about 1% v/v of an appropriate acid. Since many standards for flame AA can be of very low concentration (possibly less than 1 mg/L) it will be necessary to add extra acid to ensure that the pH remains low (between pH 1 and 2).
9. The sample must be in liquid form for analysis by flame atomic absorption. If there are particulates in solution which contain the analyte, these particulates may settle out and give an absorbance much lower than the true value would be. Small particles (less than 10 μm) can be analyzed by flame AA but large ones may not be completely atomized. It is necessary to frequently shake solutions containing particulate matter to ensure complete dispersion throughout the liquid.

Ideally solutions for analysis should be free from suspended matter.

10. Check the ionization suppression. Atomic absorption spectroscopy requires that the atoms be in their ground state. At high temperatures ionization may occur, reducing the number of ground state atoms and therefore reducing the absorbance. This especially occurs in the nitrous oxide-acetylene flame, and some of the more easily ionized elements include calcium, strontium and barium.

In order to prevent ionisation an "ionization suppressant" is added. An ionization suppressant is a high concentration of another more easily ionized element. The elements used normally are the alkaline elements (potassium or cesium). These elements have a lower ionization poten-

tial than the elements previously listed and therefore minimize their ionization by supplying an excess of electrons in the flame. Typically 5000 mg/L of potassium is added to the sample (and standards) to suppress ionization.

11. A fault in the hollow cathode lamp itself is rarely a cause of low absorbance.

Excessive Noise or Unstable Signals in Flame AA

Use the following sequence to check possible sources of excessive baseline noise. The flame is not ignited during this series of checks:

1. Use the manufacturer's recommended values for hollow cathode lamp current and spectral band width.

The baseline absorbance noise (n) is related to the light source intensity I_o by the following expression,

$$n \propto \frac{1}{\sqrt{I_o}}$$

Therefore the baseline noise decreases as the source intensity increases. Further, the intensity of the light source I_o is approximately proportional to the square of the lamp current. Therefore if the lamp current is increased then the baseline noise level decreases accordingly.

However if the increase in lamp current is too high then a phenomenon called "self absorption broadening" may occur, in which the atoms in the hollow cathode lamp absorb the light being emitted from the sputtering process which occurs in the hollow cathode itself. The result is lower absorbance and increased calibration curvature.

Lamp life is also shortened when the higher lamp currents are used. Do not exceed the maximum recommended lamp current at any time.

When a hollow cathode lamp's life has expired there will still be a glow from the lamp itself but there will be no intense light emitted from the hollow cathode. The glow surrounds the cathode, but the hollow cathode will no longer produce the light necessary for atomic absorption analyses.

The spectral band width also plays an important role in the signal-to-noise ratio. When a large spectral band width is used the signal-to-noise ratio may be excellent but the resonance line may not be isolated from other lines; thus the calibration curve may be non-linear. But if a very narrow spectral band width is used, the good resolution may not compensate for the poor signal-to-noise ratio that will occur because of the reduced light throughput.

Therefore use the manufacturer's recommended conditions for the analysis as a starting point and change the conditions according to the desired signal-to-noise ratio.

2. Incorrect alignment of the light sources and inaccurate selection of wavelength of the monochromator can increase the baseline noise level. The lamp must be set for maximum throughput, providing maximum energy, therefore obtaining minimum noise. The two knurled control knobs on the lamp quadrant allow both vertical and horizontal adjustment to be made in order to achieve maximum light throughput.

Many elements such as cobalt, iron, nickel and vanadium have complex spectra. These elements need extra care when the wavelength is being peaked. To check the wavelength accuracy use the copper hollow cathode lamp and peak on the 324.8 nm wavelength. If there is an apparent shift in the wavelength control this will normally indicate an overall linear shift throughout the full wavelength range. For example, if the copper lamp is peaked at 324.6 thus indicating a 0.2 shift, when the barium line of 553.5 nm is to be used, the true barium line will be indicated at approximately 553.3 nm.

3. In order to maximize the energy passing through the optical system the lenses and windows must also be kept clean and clear of mechanical damage. To clean the lenses of an AA-3, -4, -5 or -6 spectrophotometer the only recommended procedure is:

- Wash with a clean cloth or optical tissue moistened with ethanol.
- Dry.

Lamp windows and sample compartment windows can also be cleaned using an optical tissue which has been previously moistened with ethanol. Ensure when cleaning these surfaces that there is no mechanical damage to the surface.

4. If scale expansion is being used the baseline noise level will be expanded just as the absorbance is expanded. In a similar manner, when the concentration mode is used, the digital display may be expanded in order to achieve the desired units on the display. Remember that the baseline noise will also reflect the expansion applied. An integration time (for example 5–10 secs) can be used in order to "smooth" some of the signal fluctuations.

Note the following points:

- The maximum fluctuation in the absorbance reading with a new '75 series instrument set up for copper (no flame) should be ± 0.001 Absorbance or less. set the instrument with background correct off, and integrate repeat with time 1 sec. If the instrument has had considerable use in a laboratory, gradual deterioration from this specified noise level can occur. With older instruments (not the '75 series) the noise level could be observed on a recorder chart and would typically show less than ± 0.002 Absorbance on the minimum damping position of the instrument when set up for copper.
- Different elements exhibit different noise levels depending on the intensity of the light source. At low wavelengths, for example, the energy from the light source is lower, therefore a higher EHT (extra high tension), is required on the photomultiplier tube. With an element such as selenium or zinc, the baseline noise levels would be greater than that shown for copper. Hollow cathode lamps which are relatively intense include calcium, lithium, magnesium, aluminium and silver. Hollow cathode lamps of relatively weak intensity (and therefore higher baseline noise) include cobalt, iridium, iron, nickel and bismuth.
- As mentioned previously hollow cathode lamps will eventually fail and must be replaced. When there is no light output from the lamp and all conditions have been checked, for example, that the lamp is turned on to the recommended current and aligned, the lamp should be replaced. The lifetime of the lamp varies according to the element in the cathode and the operating current. The hollow cathode lamps are warranted for 5,000 milli-ampere hours of operation at or below the recommended operating current. milli-ampere hours are calculated as the product of the hours of use and the current. For example, if a lamp is being operated at 5 mA for 100 hours the number of milli-ampere hours is 500.

Excessive Noise or Unstable Signals in Flame AA (Only With the Flame On)

At certain wavelengths the flame will absorb light. If an analysis is being carried out in this wavelength region, some increase in noise level will normally occur. However, it is not possible to specify the increase in baseline noise level to be expected. If the instrument has been correctly set up as described and the noise level is considered excessive only with the flame on, a number of checks can be made to determine the cause.

Burner Position

The position of the burner with respect to the optical path can play an important part in the level of baseline noise. For example, as the burner is lowered, the viewing position is higher in the flame where it may be unsteady thus increasing the baseline noise. Conversely, if the burner is too high and largely blocking the light path, the amount of energy passing through the system is decreased; therefore the noise level is increased and the atomic absorption signal will be reduced. In order to obtain the lowest noise level the burner must be carefully aligned as described earlier.

Flame Stability and Flame Absorption

Because the flame atomisation system is dynamic, there is a continuous fluctuation in the flame itself. These fluctuations are due to movement of the flame caused by draughts or by insufficient mixing of the gases. Continuous change in flame absorption can affect the amount of light being passed through the sample compartment into the monochromator at certain wavelengths. This can introduce a component of noise which is independent of light intensity. In order to prevent as much of this flame noise as possible, always ensure that the flame draught shields are correctly installed to prevent local air draughts in the laboratory from disturbing the flame. Otherwise the flame may become unstable to the extent that extra flame noise is introduced into the measurement. This would be especially important at those (low) wavelengths where the flame absorbs such as with analysis of arsenic, selenium, antimony, tellurium, zinc, lead.

Before the instrument is used in an analysis, allow the hollow cathode about a five minute warm-up period if highly accurate measurements are required. A longer period may be necessary with single beam instruments to minimize drift in the baseline. Also allow the burner to warm up for about 5-10 minutes before use. A nitrous oxide-acetylene burner will need the longer time to equilibrate at operating temperature before highly accurate measurements are taken. These measures prevent a drift in the absorbance reading, especially with single beam instruments.

Gas Pressures and Flows

It is important that, if air is being supplied from a compressor, an air filter must be fitted between the compressor and the gas control module. A liquid trap must also be fitted in this line as moisture in the system affects the internal tubing and other components of the gas control unit. The presence of liquid in the gases can yield highly irregular results. Nitrous oxide and acetylene should be sufficiently pure to prevent any impurities causing problems with the analysis.

Acetylene cylinders must not be used when the pressure falls below 100 psi (700 kPa). If the cylinder pressure does drop below 100 psi acetone can be transferred through into the gas control system causing damage which is potentially hazardous. Presence of acetone in the acetylene can also result in a change in the atomic absorption signal.

Acetylene must be purchased from the supplier packaged with acetone. Linde Division of Union Carbide Corporation offer a grade of acetylene described as "Purified Grade". This has another solvent as its base instead of acetone. The solvent used in this package can damage the instrument. Therefore ensure that the acetylene used in atomic absorption spectrophotometers is the acetone based package.

Always use the manufacturer's recommended gas pressures in the line to the instrument. Irregular changes in gas flows can result in poor analytical performance from the instrument.

Nebulizer and Burner

Both the nebulizer and the burner should be thoroughly clean and free from any blockages due to salts etc. They should be cleaned as described in the operation manual before proceeding with the analysis.

Atomic Emission

High concentrations of elements such as calcium, strontium and barium and certain rare earth elements can produce high atomic emission signals when analyzed in a nitrous oxide-acetylene flame. This atomic emission occurs at the same wavelength as the atomic absorption process, and the high level of light falling on the photomultiplier can result in some increase in signal noise level. In order to minimize this problem it is necessary to increase the lamp current to produce a higher source intensity, and thus to reduce the EHT applied to the photomultiplier.

Measurements Using a Background Corrector (Continuum Lamp)

A background corrector using a continuum light source (hydrogen lamp or deuterium lamp) is necessary when there is a significant amount of non-atomic (or background) absorption present in the measurement. To achieve successful background correction, especially with graphite furnace atomization, the continuum lamp must be aligned correctly and the intensity must be matched to that of the element source (hollow cathode lamp or electrodeless discharge lamp).

The operation manual describes the procedure for setting up a background corrector. To obtain the approximate position for the background corrector, use a business card or piece of paper to overlap the two light beams. Then follow the instructions in the manual. At times the continuum lamp may be too weak or too great in intensity to match the hollow cathode or EDL source intensity.

If the continuum light source is too intense for the hollow cathode lamp, then reduce the spectral band width. In many cases this will enable the intensity of the two beams to match. The reason lies in the fact that the energy from the continuum light source increases with the square of the spectral band width, whereas the energy of the (narrow) atomic spectral line from the hollow cathode lamp increases linearly with the spectral band width.

It also follows that the converse applies; that is, if the hollow cathode lamp intensity is too great in comparison with the continuum lamp, then increase the spectral band width. This simple technique will often permit matching of the intensity of the two lamps, and a background corrected measurement to be carried out.

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